Gulf Coast Aerosol Research and Characterization Program (Houston Supersite)

PROGRESS REPORT

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University of Texas at Austin

Submitted by:

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EPA Agreement No.: **R-82806201**

Title: **Gulf Coast Aerosol Research and Characterization Study**

Investigators: **Dr. David Allen (PI) and Dr. Matthew Fraser (Co-PI)**

Institutions: **University of Texas and Rice University**

Research Category: **Air Quality/Fine Particulate Matter**

Project Period: **01/15/00-11/30/03**

Objective of Research: **Characterize fine particulate matter and fine particulate matter formation processes in Southeast Texas**

Progress Summary/Accomplishments:

During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focussed on gas phase chemistry (the Texas Air Quality Study). Selected preliminary findings are presented in this report.

During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focussed on gas phase chemistry (the Texas Air Quality Study). Selected preliminary findings are presented in this report. Specifically, preliminary results of the single particle mass spectrometry and the aerosol quality assurance system are presented.

I. Single particle mass spectroscopy of samples collected at Houston Regional Monitoring Network Site 3 (HRM3), University of Delaware,

Denis J. Phares, Kevin P. Rhoads, Murray V. Johnston, Anthony S. Wexler

The deployment of Rapid Single-particle Mass Spectrometer (RSMS-II) at the HRM3 site during the Supersite intensive sampling period affords an exciting glimpse into particle formation and evolution processes in urban environments. Data collection and analysis have been developed to the point that new conclusions concerning ultrafine aerosol in the urban Houston atmosphere have already been obtained within only several months of the field campaign. This progress report will briefly outline instrument operation and data analysis procedures, while presenting some results and important conclusions that may be inferred from these results.

Instrument Summary

Since RSMS-II has previously been described in detail (1,2), only the main points will be summarized here. The instrument measures the aerodynamic diameter and composition of individual ultrafine particles. Particles are size-selected using an inlet, which selectively focuses a narrow aerodynamic size range to the ion source region of a time-of-flight mass spectrometer. A pulsed excimer laser (193 nm) is focused to the center of the ion source region, ablating particles that coincide with the active laser volume. The ions formed in the process are accelerated into a time-of-flight drift tube where they separate based on molecular weight. A microchannel plate at the end of the drift tube measures the ion current, thereby yielding a mass spectrum of the original

particle. The difficulty forming negative ions from laser ablation of ultrafine particles (3) made positive ion spectra acquisition the chosen mode of study.

Sampling was continuous for most of the intensive study starting on August 23rd and ending on September 30th. The sampling procedure involved collecting mass spectra of particles at a selected aerodynamic size until it was determined that a statistically significant data set had been obtained. The instrument parameters were subsequently adjusted to select another particle size. When the entire desired range of particle sizes was covered, a new size scan was immediately started. Nine aerodynamic sizes were selected for the present study to optimize comparison with speciation results from bulk impactor samples: 35, 50, 70, 100, 140, 170, 320, 590, and 1140 nm. A single scan through the entire size range lasted roughly 110 minutes.

Site

RSMS-II was deployed at the HRM3 site located in Channelview, TX – east of Houston and less than 0.5 miles north of the ship channel. The immediate vicinity of the monitoring site can be characterized as very industrial – laden with chemical plants, oil refineries, and incinerators. The site is sandwiched between a very active railway segment to the south and the PVS chemical plant to the north. It is therefore reasonable to expect that the ultrafine aerosol measured at HRM3 are newly formed through nucleation of freshly emitted gas phase pollutants or directly emitted in the aerosol phase. The proximity of the dominant sources reduces the probability of significant aerosol processing in the atmosphere, unlike sites upwind or far downwind of the sources.

Data Analysis

Since single-particle instruments obtain tens of thousands of mass spectra during typical field campaigns, it is necessary to employ automated schemes to sort and classify the spectra allowing meaningful information to be extracted. The neural networks algorithm, ART-2a, was chosen for the present study because of previous successful application to data obtained with RSMS-II (4). During the intensive study, ART-2a was used to determine whether a statistically significant number of particles had been obtained before moving on to the next aerodynamic size in a scan. Particles were thus

classified in real time allowing a preliminary class distribution, which determined the need to continue sampling at the same size or move on to the next size. Since the end of the intensive sampling period, the entire set of mass spectra was reanalyzed with the neural networks algorithm, yielding a new complete class distribution.

Results and Preliminary Conclusions

Over 30,000 mass spectra were obtained over the course of 5 weeks during the intensive sampling period. The ART-2a algorithm identified over 60 total classes of particles. However, only 6 of these comprised 93% of the total particles measured. These classes were labeled based on characteristic ion peaks in the mass spectra and are listed in Table 1. The obtained classifications are very different from those obtained by RSMS-II in the Atlanta, 1999 Supersite campaign, where more than 74% of measured particles were organic carbon. This indicates the dominant influence of the local sources, which were mainly combustion sources close to the Atlanta site.

Since RSMS-II obtains particle spectra in real time, it is possible to correlate the detection of a specific class with wind direction as well as particle size. This information facilitates accurate source determination. Some of the particle classes were indeed directional in nature. A class of Zinc-containing particles, for example, comprised 1.6% of total measured particles, and appeared exclusively when the wind was blowing from the south-southeast. The Aliphatic Amine class appeared mainly when the wind was blowing from the east. In general, a larger variety of particle types were observed when the wind was blowing from the south – the direction of the ship channel and the factories and refineries concentrated south of the ship channel.

Perhaps the most surprising observation from the obtained class-resolved size distributions is the abundance of ultrafine Silicon/Silicon Oxide particles – as small as 35 nm in aerodynmic diameter. The extremely small size of these particles suggests formation from an incineration process, but, at this point, the origin of these particles is not known. Even more surprising is that they were present steadily throughout the intensive and exhibited no wind directionality.

Although the major particle classes represent the typical composition of ultrafine aerosol at HRM3, the minor particle classes may provide important information

concerning transient plumes that passed through the site. More analysis is needed to determine the significance of all of the minor classes; but some have already exhibited some interesting characteristics. One minor class, for example, contained a large lead (Pb+) peak and a significant unidentified peak centered at 242 amu – perhaps a lead salt. This particular particle class appeared only on August 31st and September 1st. Since the particle class never reoccurred, it might be considered a transient emission, rather than a steady one. A material that is present in ultrafine aerosol for a short time may not easily be detected using bulk techniques; yet may still produce significant health and environmental effects.

Class Label	**Percent of total**
Potassium	31%
Silicon/Silicon Oxide	30%
Carbon	16%
Sodium/Potassium	7.5%
Iron	6.1%
Aliphatic Amines	2.8%

Table 1: Major Particle Classes

References

(1) R.V. Mallina, A.S. Wexler, K.P. Rhoads and M.V. Johnston, *Aerosol Sci. Technol.* 33, 87-104 (2000).

(2) D.J. Phares, K.P. Rhoads and A.S. Wexler, *Aerosol Sci. Technol.*, in review.

(3) P.G. Carson, A.S. Wexler and M.V. Johnston, *Rapid Commun. Mass Spec.* 11, 993-996 (1997).

(4) D.J. Phares, K.P. Rhoads, A.S. Wexler, D.B. Kane and M.V. Johnston, *Anal. Chem.*, in review.

II. Aerosol Quality Assurance System , State University of New York,

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The goal of this component of the Houston Supersite program was to serve as a test bed for a aerosol quality assurance system. The Standard Aerosol System I (SASI) provided a consistent and reproducible sample aerosol, allowing for a data intercomparison between a variety of instruments. The system was designed to work with instruments that measure number size distributions (Electrical Mobility Spectrometer, Optical Counter), chemical composition (PILS, Aerodyne MS), and size and composition (single particle MS), though during Texas 2000 SASI was also successfully used with continuous gravimetric instruments. Eight organizations participated in the intercomparison study with 17 different instruments.

Of the eight organizations participating, two have submitted the final results for their data. Two more organizations have submitted partial results. Four organizations have not yet submitted results. Some preliminary observations are given below.

Of 9 instruments presented with a monodisperse aerosol containing polystyrene latex spheres (PSL) with a diameter of approximately 300 nm, 5 were able clearly to detect the particle.

Of 9 instruments presented with a polydisperse aerosol containing PSLs of 5 different sizes in the range from approximately 100 nm to 600 nm, one instrument detected all 5 particle sizes, and seven instruments detected some of the particle sizes.

Of 10 instruments presented with a polydisperse aerosol containing an inorganic and an organic compound, 9 instruments were able to detect a broad distribution of particles sizes. Seven of these instruments had compound identification capability. Of these 7, 5 were able to identify the inorganic compound and 2 were able to identify the organic compound.

Again, these observations are based on preliminary data only and are subject to change as the data collection process continues.

Data collection and analysis will remain the focus of subsequent work. The time required for data collection is highly dependent on the researchers who participated in the

study. In many cases, extensive data work-up is required before the results can be translated into a format conducive to intercomparison. For some, the shear volume of data generated necessitates many months of data conversion. Intercomparisons of the data will be an ongoing process as the information is received.